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Structural and magnetic properties of a series of low doped $Zn_{1-x}Co_xO$ thin films deposited from Zn and Co metal targets on (0001) Al_2O_3 substrates.

A. Fouchet, W. Prellier*, P. Padhan, Ch. Simon and B. Mercey

Laboratoire CRISMAT, CNRS UMR 6508, 6 Bd du Marechal Juin, F-14050 Caen Cedex, FRANCE.

V.N. Kulkarni† and T. Venkatesan

Center for Superconductivity Research, University of Maryland, College Park, MD 20742-4111, USA

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Abstract

We report on the synthesis of low doping $Zn_{1-x}Co_xO$ ($0 < x < 0.1$) thin films on (0001)-Al_2O_3 substrates. The films were prepared in an oxidizing atmosphere, using the pulsed laser deposition technique starting from Zn and Co metallic targets. We first studied the influence of the strains of ZnO and their stuctural properties. Second, we have investigated the structural and the magnetic properties of the $Zn_{1-x}Co_xO$ films. We show that at low doping, the lattice parameters and the magnetization of the $Zn_{1-x}Co_xO$ films depend strongly on the Co concentration.

*prellier@ismra.fr

†on leave from Indian Institute of Technology, Kanpur, India

I. INTRODUCTION

Diluted Magnetic Semiconductors (DMS) of III-V or II-VI types have been obtained by doping semiconductors with magnetic impurities (Mn for example)[1,2]. These materials are very interesting due to their potential applications for spintronics[3]. However, the low Curie temperature (T_C) has limited their interest[4] (for example $Ga_{1-x}Mn_xAs$, with $x = 5.3\%$ has a $T_C = 110K$[5]). Based on the theoretical works of Dietl *et al.*[6], several groups[7] have studied the growth of Co-doped ZnO films[8–11] which is a good candidate having a high T_C[6]. Using pulsed laser depositions (PLD), Ueda *et al.* reported ferromagnetism (FM) above room temperature[8], while Jin *et al.* found no indication of FM by utilizing laser molecular beam epitaxy[9]. This controversy between research teams may result from the growth method used and/or from the growth conditions (oxygen pressure, deposition temperature, etc...). In the particular case of the PLD technique, it may also arise from the targets preparation and this parameter has never been considered up to now. One of the reason is that the control of the dopant incorporation would be quite difficult to obtain using a pre-doped ceramic oxide target[12]. This is a crucial point since the properties of the DMS are very sensitive to the percentage of dopant[13]. The homogeneity of dopant incorporation as well as the precise control of the growth might be responsible for the changes in the physical properties of the films obtained by the different groups. Thus, we have recently developed an accurate method to grow the $Zn_{1-x}Co_xO$ films with a precise doping by using an alternate deposition starting from Zn and Co targets. Using this procedure[14], we have been able to observe ferromagnetism at room temperature in one sample having the composition $Zn_{0.95}Co_{0.05}O$ confirming previous results[8] but in contrast to others[9]. In this paper, we have grown a series of $Zn_{1-x}Co_xO$ films with very low doping of Co. We have studied the structural and magnetic properties of the films and our results are reported in this communication.

II. EXPERIMENTAL

The $Zn_{1-x}Co_xO$ films were grown using the pulsed laser deposition technique. Metal Zinc (99.995%) and Cobalt (99.995%) targets were used as purchased (NEYCO, France) without further preparations. The films are deposited using a KrF laser ($\lambda = 248mm$)[14] on (0001) Al_2O_3 substrates (in this paper, we used the three-index notation instead of the four-index one[15]). The substrates were kept at a constant temperature in the range 500°C-750°C during the deposition which was carried out a pressure around $0.1Torr$ of pure oxygen. After deposition, the samples were slowly cooled to room temperature at a pressure of $225Torr$ of O_2. The deposition rate is $3Hz$ and the energy density is close to $2J/cm^2$. The composition of the film was checked by Energy Dispersive Scattering and Rutherford Backscattering Spectometry (RBS).

The structural study was done by X-Ray diffraction (XRD) using a seifert XRD 3000P for the $\Theta - 2\Theta$ scans and the $\omega-$scan to evaluate the full-width-at-maximum (FWHM). An X'Pert Phillips was utilized for the *in-plane* measurements obtained from the (101) reflection. Ion Channeling technique (with 2 MeV He^+ ions) was used to study the epitaxial nature of the films.

Magnetization (M) was recorded as a function of the temperature (T) and the magnetic field (H) in a SQUID magnetometer.

III. RESULTS

ZnO thin film was deposited using the optimal conditions found previously[14]. The films are highly crystallized as seen from the sharp diffraction peaks (Fig.1) and the FWHM of the rocking curve close to 0.25° (Fig.4). The two diffractions peaks observed around 34.48° and 72.66° are characteristic of the hexagonal ZnO wurtzite, the c-axis being perpendicular to the substrate plane. The out-of-plane lattice parameter is calculated to be $0.52nm$ which corresponds to the theoretical bulk one[16]. The epitaxial relationships between ZnO films

and Al_2O_3 substrates are determined using asymmetrical XRD. The inset of Fig.1 displays the $\Phi-$scan both of the ZnO films obtained from the (101) planes and the Al_2O_3 substrate obtained from the (104) planes. The peaks belonging to the film are separated by 60°, indicating a six-fold symmetry in agreement with the hexagonal structure of ZnO whereas the peaks of the sapphire substrate are separated of 120° indicating a three-fold symmetry in agreement with the rhombohedral symmetry of Al_2O_3. Note that 30° spacing between the diffraction peaks of the film and those of the substrate indicate a rotation of 30° between the in-plane axes. In order to obtain additional information, on the structural properties of the ZnO films, we have determined the strains of the optimized film. This technique used the distance between atomic plane of a crystalline specimen as an internal strain gage[17]. Using this model, we minimized the strains of the ZnO film by changing the growth conditions[14]. At a temperature of $600°C$ under $0.1Torr$ of O_2, we found[18] that the value of residual stress (σ) along the in-*plane* direction ($\sigma_\Phi = 150MPa$) is about the same value along the *out–of-plane* direction ($\sigma_\perp = 150MPa$). Such values are in agreement with previous report[19]. The study of the ($10l$) planes indicates a concentration gradient along the *out-of-plane* direction. In other words, the strains is larger near the interface and decreases along the *out-of-plane* direction as the thickness increases. Indeed, when the thickness of the film, the substrate-induced strain becomes lower and the lattice parameters of films become closer to the value of the bulk. Moreover, the positive slope[18] indicates an extensive stress *in-the-plane* of the substrate which is in agreement[20] with the decrease of the *out-of-plane* lattice parameter as compared to the bulk value[16].

These conditions have been used to grow the $Zn_{1-x}Co_xO$ films with various doping x. An example of the ion backscattering channeling data for $Zn_{1-x}Co_xO$ (x=4%) is given in Fig.2. The observed minimum yield $\chi_{\min}$ of ≈5% for channeling reflects good quality of the film, thereby indicating optimum growth of $Zn_{1-x}Co_xO$ films. Note also that a surface peak of Co is seen which reveals that the top layer (about $400\mathring{A}$) has large amount of Co (11%). The channeling spectrum also shows the Co signal. This indicates that the Co in this layer has not gone substitutional. Fig.3 shows the $\Theta - 2\Theta$ scans recorded around the

002 reflection in the the range $34 - 35°$. As the Co content is increasing there is a shift toward the high angle, indicating a decrease of the *out-of-plane* lattice parameter up to 1.6%. Above this value, the position of the diffraction peak is moving toward the low values of 2Θ, leading to an increase of the lattice parameter up to 9%. Then, the *out-of-plane* lattice parameter becomes constant[14] (not show in this graph). To explain this results, we consider the ZnO bulk wurtzite structure, where zinc (Zn^{2+}) is in tetrahedral site with a ionic radius of $0.6\mathring{A}$[21]. The substitution of the Zn^{2+} with Co^{2+} (ionic radius: $0.58\mathring{A}$[21]) leads to a compression of the bulk structure and a decrease of the lattice parameters. On the contrary, a higher coordination number of Co^{2+} leads to an ionic radius of Co^{2+} larger than the ionic radius of Zn^{2+}. In this configuration, Co^{2+} would be in an interstitial site inducing an expansion of the structure (and an increase of the lattice parameters) and thus, an increase of defects. In the thin film, due to the substrate-induced strains, this will lead to a decrease of the *out-of-plane* lattice parameter (up to 1.6% of Co) and then to an increase of this parameter ($1.6\% < x < 9\%$). This explanation (substitution and then interstitial Co) is also confirmed by looking at the evolution of the FWHM of the rocking curve as a function of the Co content (see Fig.4) where the same tendancy is observed. For very low doping of Co ($0 < x < 1.6\%$), the FWHM is slightly decreasing up to 1.66% of Co. Above this value ($x > 1.6\%$), the FWHM increases when the Co content is also increasing indicating that for these values of doping, the films are less oriented and/or contained more defects.

We investigated the magnetic properties of these thin film samples. Fig.5 shows the $M(T)$ recorded for various $Zn_{1-x}Co_xO$ film. The films at low doping of Co (1.6% and 6.6%) clearly evidence a ferromagnetic state with a Curie temperature respectively around $150K$ and $300K$. For the other concentration of Co, the situation is more confusing. We have performed $M(H)$ at different temperatures but we did not observed any hysteresis. We also measure the magnetization in very low doping ($x < 1.6\%$) but the signal of the substrate is too high.

We discuss now the possibility of the Co clusters in our films. The transition from the ferromagnetic state to the paramagnetic state is clearly seen, suggesting that the metallic

Co clusters (the T_C of the metal Co clusters is above 1000K) are not responsible for the effect observed at 300K[10,11]. Moreover, the saturation moment (0.7 μ_B/mole Co) is very weak compared to 1.7μ_B of metallic Co[0], suggesting that the Co state should be close to Co^{2+}. We believe that this is due to the technique used in the study where not only the conditions of the deposition minimize the strains but also the alternate deposition from the two targets favors the homogeneity of the doped films. Moreover, it has been seen that the low temperature (600°C is our case) of deposition leads to homogenous films[10].

IV. CONCLUSION

In conclusion, we have developed an alternative method for the growth of pulsed laser deposited oxide thin films. This method permits an accurate control of the dopant in the matrix. Firstly using this procedure, we have deposited high quality $Zn_{1-x}Co_xO$ thin films on Al_2O_3 (0001) substrates with a low doping of Co. Secondly, we have also studied the evolution of the structure and the magnetic properties of the films for various Co concentration. We suggest that the incorporation of Co inside the wurtzite structure leads to an increase of interstitial defects while the epitaxial defects decrease. Finally, the growth of these ferromagnetic films opens the route for the fabrication of spin-based electronics since this original method can be used to grow various oxide thin films.

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Figures Captions:

Figure 1: Room temperature $\Theta - 2\Theta$ XRD pattern of typical ZnO film. The inset depicts the Φ-scan of the film and the substrate respectively recorded around the {101} and {104} family peak.

Figure 2: The 2 Mev He^+ Rutherford Backscattering random and channeled spectra of $Zn_{1-x}Co_xO$ film (x=4%).

Figure 3: Room temperature $\Theta - 2\Theta$ XRD pattern of a series of $Zn_{1-x}Co_xO$ film. The percentage of Co is indicating.

Figure 4: Rocking curve (ω-scan) recorded around the 002 reflection for a series of $Zn_{1-x}Co_xO$ film.The percentage of Co is indicating. The FWHM is increasing from 0.23° for pure ZnO to 0.43° for $Zn_{1-x}Co_xO$ with x=5%.

Figure 5: $M(T)$ of a series of $Zn_{1-x}Co_xO$ film measured sith a field of $2000Oe$. The percentage of Co is indicating.

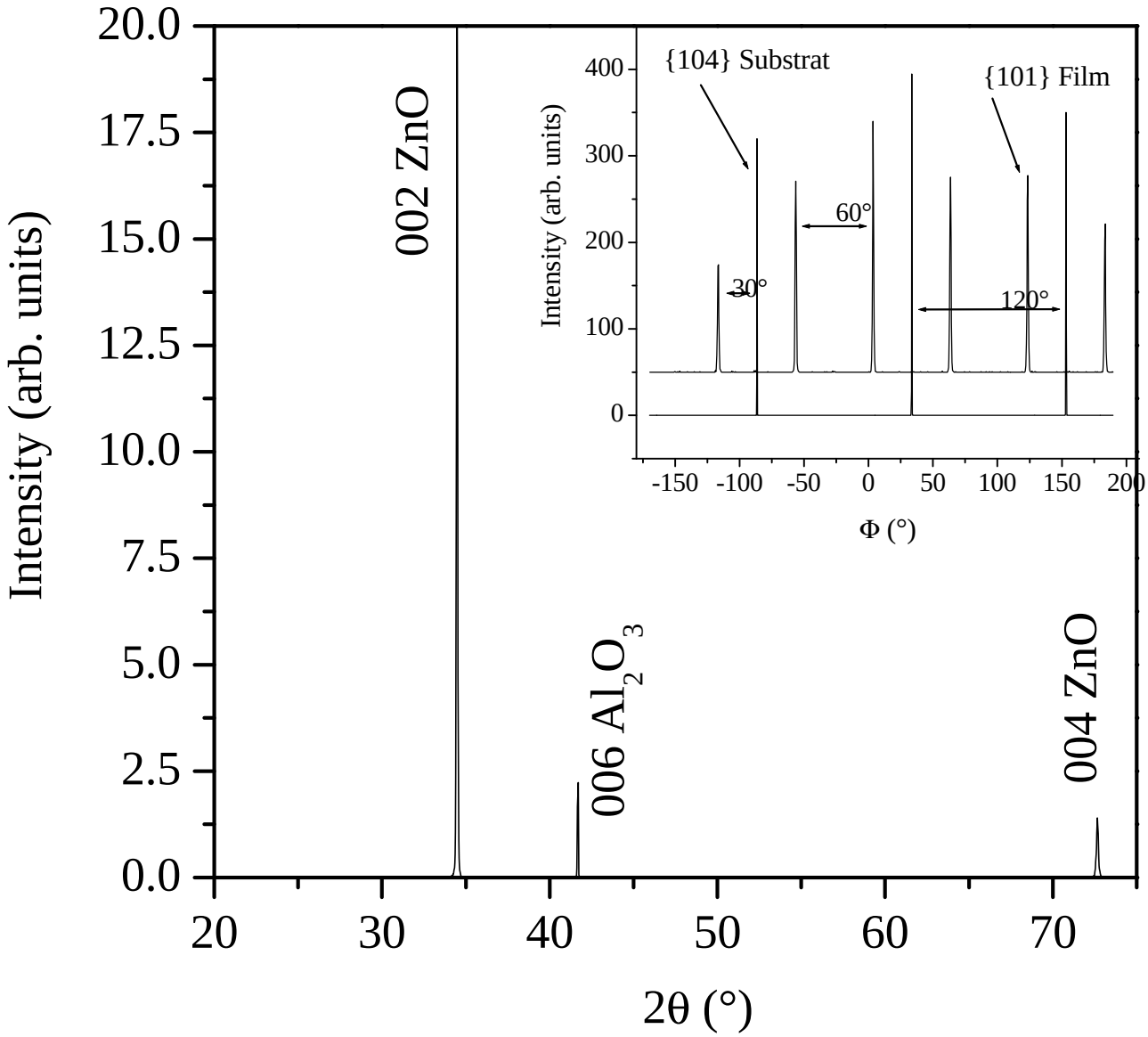

Figure 1

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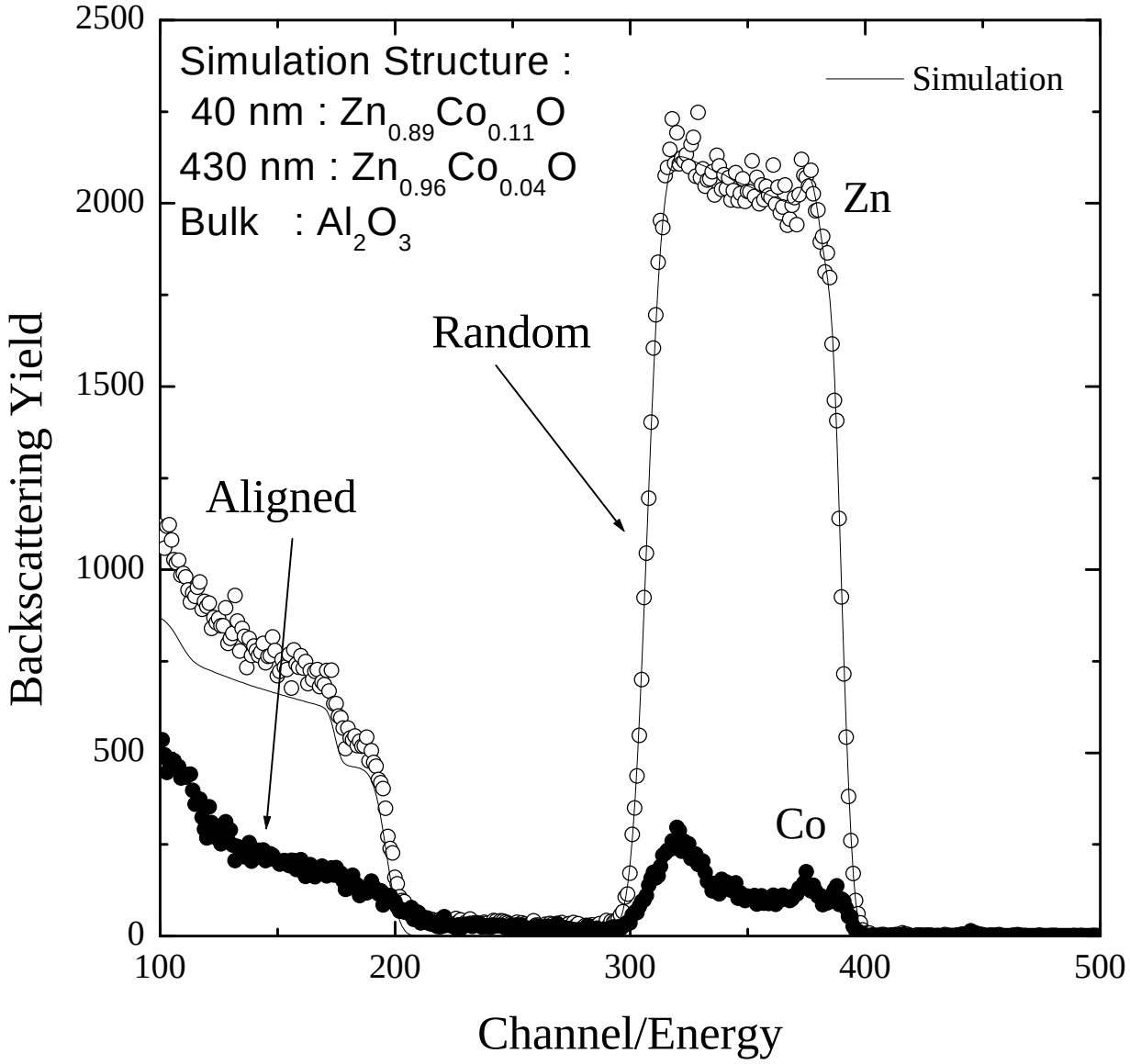

Figure 2

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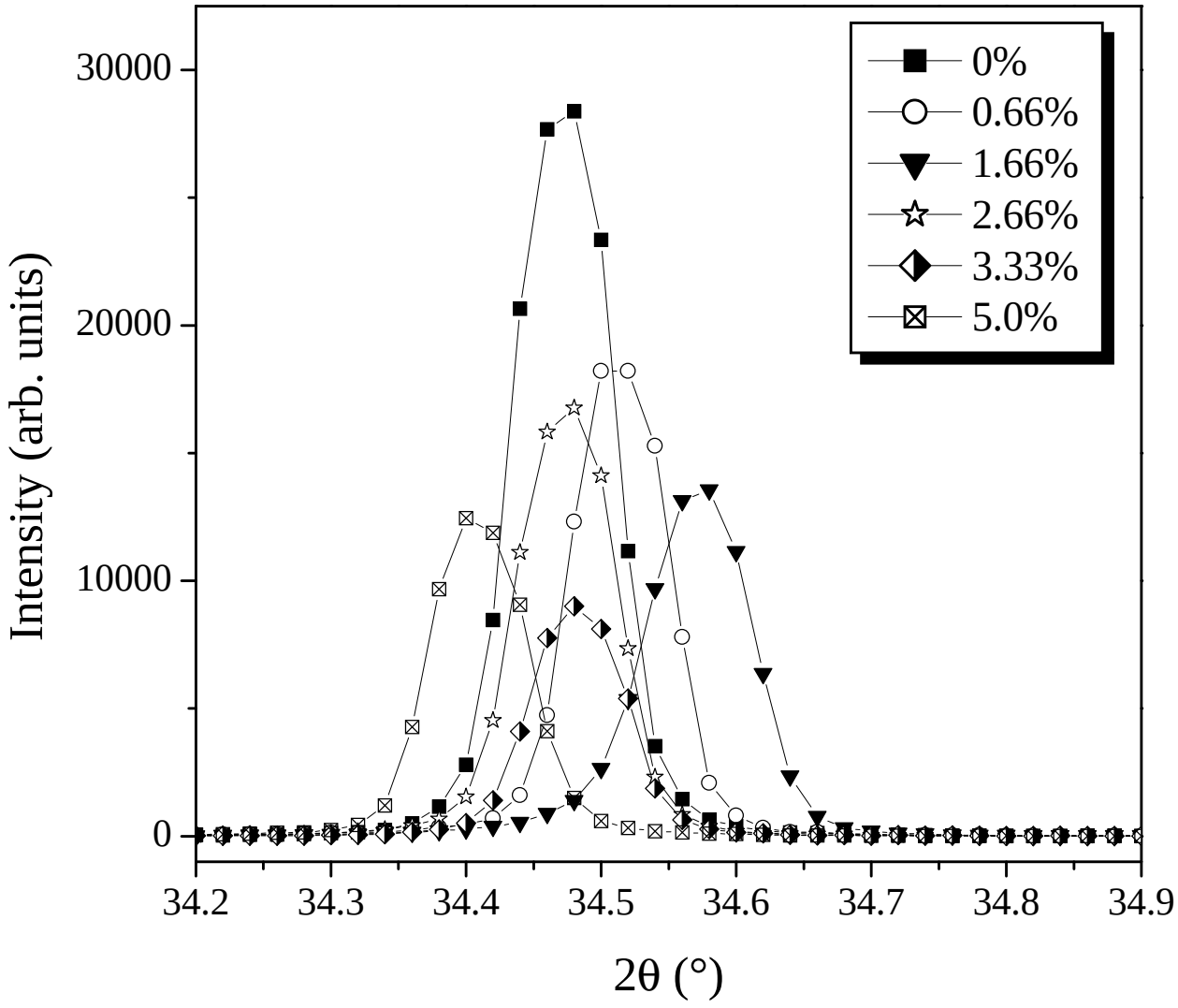

Figure 3

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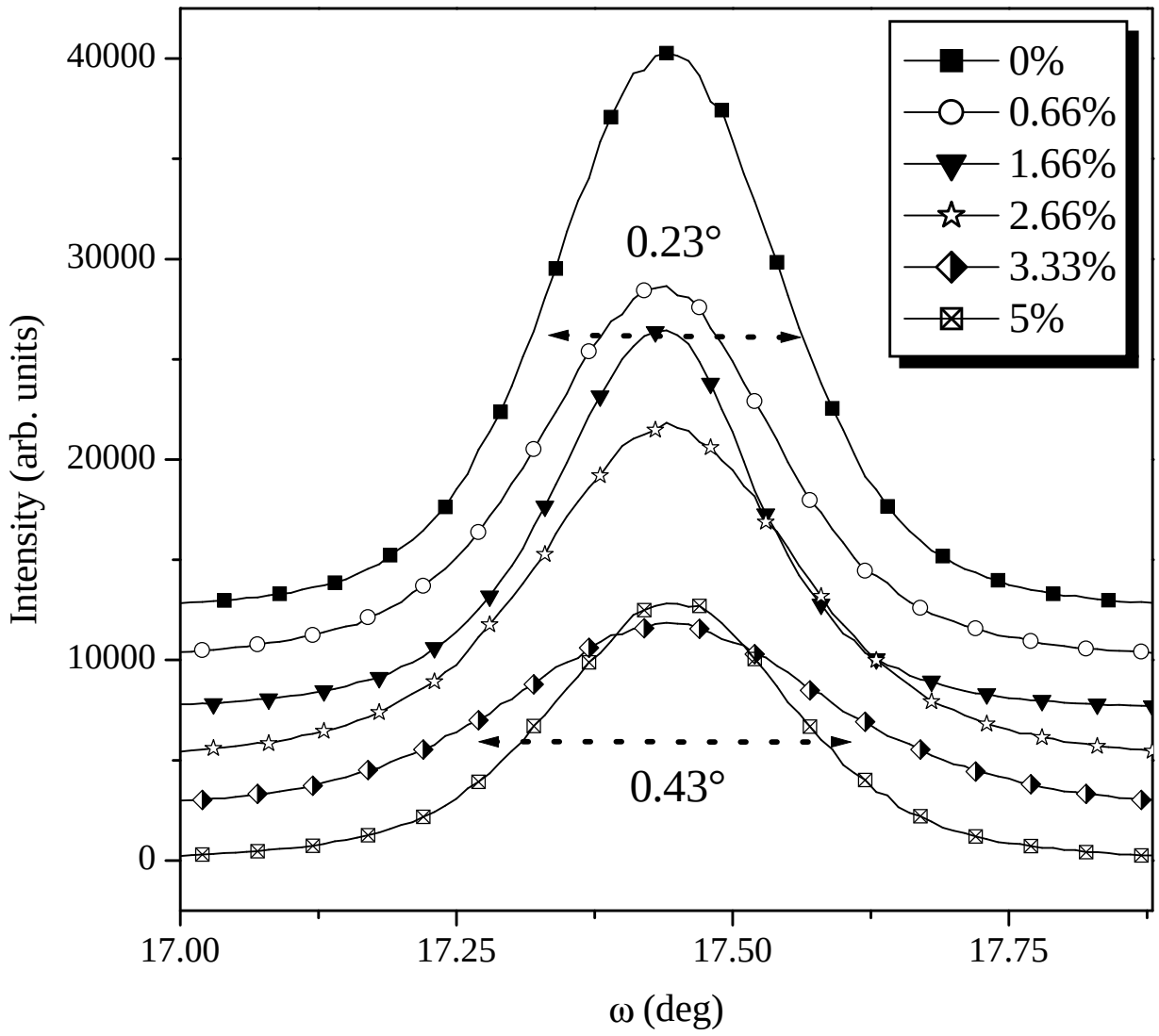

Figure 4

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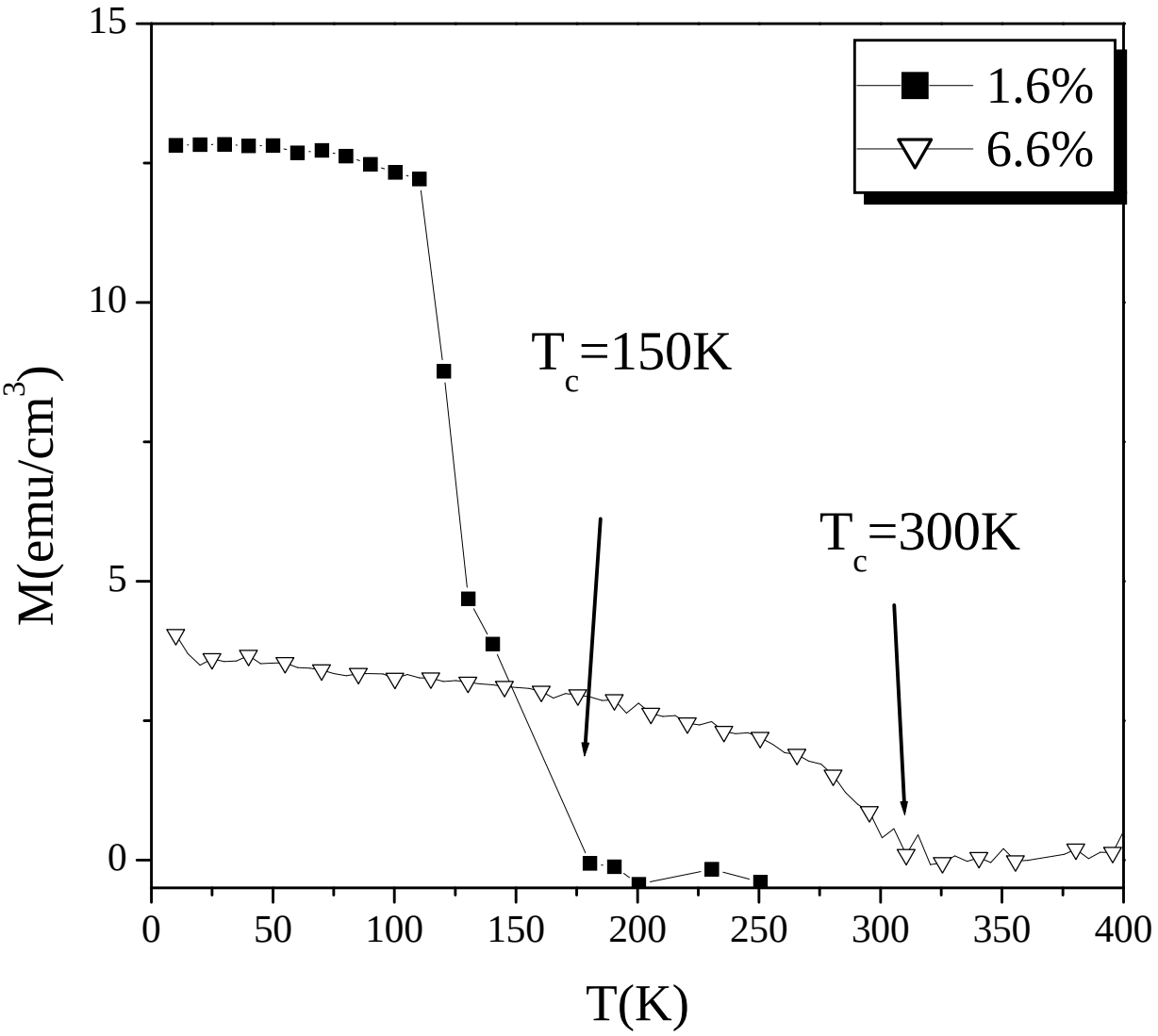

Figure 5

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